DATA EVALUATION RECORD

STUDY 3

CHEM 031401 Dichloroprop §163-1
CAS No. 15165-67-0
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 44028901
Wells, D. F. 1996. 2,4-DP-p: determination of batch-equilibrium adsorption and desorption coefficients following FIFRA guideline §163-1. Laboratory Project No. 13021.0495.6105.710. Unpublished study performed by Springborn Laboratories, Inc., Wareham, MA; and submitted by 2,4-DP Task Force, Research Triangle Parkway, NC.

DIRECT REVIEW TIME = 55 Hours

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acetone), at nominal concentrations of 1.2, 0.60, 0.30, and 0.15 mg/L, were added to glass centrifuge tubes containing samples (8 g) of air-dried, sieved (2 mm) clay, sand, sandy loam, and Timmerman sandy loam soils; triplicate tubes were prepared for each soil type/treatment rate combination (p. 17). The soil:solution slurries (1:5, w:v) were mechanically shaken for 18 hours at 20 ± 2 °C (pp. 13, 17). Control tubes without soil containing treated $CaCl_2$ solution were equilibrated along with the sample soil:solution slurries. Following the equilibration period, samples were centrifuged and the supernatant was decanted. Aliquots of the supernatant from each sample were analyzed for total radioactivity by LSC (pp. 14, 18); the detection limit was 0.58 µg/L (p. 15).

For the desorption phase of the study, pesticide-free 0.01 M $CaCl_2$ solution (5 mL less than recovered in the adsorption phase) was added to the centrifuge tubes containing soil from the adsorption phase of the study (p. 25; see Comment #2). The samples were shaken for 48 hours and maintained as previously described. Following the equilibration period, samples were centrifuged and the supernatants were decanted. Aliquots of the supernatant from each sample were analyzed for total radioactivity by LSC. An additional desorption was conducted for the clay and sandy loam soils. Following the initial desorption phase, additional pesticide-free $CaCl_2$ solution was added to the two soils and the samples were shaken for 18 hours. Following the equilibration period, the samples were centrifuged and the supernatant was decanted. Aliquots of the supernatant were analyzed for radioactivity by LSC. The post-extracted clay and sandy loam soils were analyzed for total radioactivity by LSC following combustion.

An independent stability test was conducted to determine if the parent compound was stable under test conditions (p. 15). Aliquots of 0.01 M $CaCl_2$ solution treated with uniformly phenyl ring-labeled [^{14}C]dichloroprop, at a nominal concentration of 1.20 mg/L, were added to three glass centrifuge tubes containing samples of each soil. The soil:solution slurries (1:5, w:v) were mechanically shaken for 36 hours and the supernatant was decanted (p. 16). Aliquots of the supernatant were analyzed by reverse-phase HPLC (Metachem Spherisorb ODS-2 column) using a mobile phase gradient of 0.1% trifluoroacetic acid (in reagent water):acetonitrile (60:40 to 40:60 to 0:100, v:v) with radioactive flow detection; samples were co-chromatographed with nonradiolabeled reference standards (pp. 16, 17). The data indicated that the parent compound was stable; 96.6-100% (based on individual replicates for all soils) of the recovered radioactivity was present as parent (Table III, p. 31).

DATA SUMMARY

Uniformly phenyl ring-labeled [^{14}C]dichloroprop (radiochemical purity 98.3%), at nominal concentrations of 1.2, 0.60, 0.30, and 0.15 mg/L, was studied in clay, sand, and two sandy loam soil:solution slurries (1:5, w:v) that were equilibrated for 18 hours at 20 ± 2 °C. Freundlich K_{ads} values were 0.79 for the clay soil, 0.25 for the sand soil (see

Comment #4), 1.7 for the sandy loam soil (3.5% o.m.), and 0.41 for Timmerman sandy loam soil (0.9% o.m.; Tables V, VII, IX, XI, pp. 33, 35, 37, 39); corresponding K_{oc} values were 83.7, 32.7, 81.5, and 78.2 mL/g. Respective 1/N values were 0.87, 0.59, 0.84, and 0.91 for adsorption. The reviewer-calculated coefficient of determination (r^2) values for the relationships K_{ads} *vs.* organic matter, K_{ads} *vs.* pH and K_{ads} *vs.* clay content were 0.92, 0.48 and 0.002, respectively. Freundlich K_{des} values determined after a 48-hour equilibration period were 1.3 for the clay soil, 0.17 for the sand soil, 3.1 for the sandy loam soil, and 2.5 for Timmerman sandy loam soil (Tables VI, VIII, X, XII, pp. 34, 36, 38, 40); corresponding K_{oc} values were 143, 21.9, 149, and 474 mL/g. Respective 1/N values were 0.59, 0.28, 0.72, and 0.84 for desorption.

During the 18-hour equilibration period, 13.7-17.3% of the applied radioactivity was adsorbed to the clay soil (across all application levels), 4.1-9.7% was adsorbed to the sand soil, 25.0-32.4% was adsorbed to the sandy loam soil, and 6.9-9.4% was adsorbed to the Timmerman sandy loam soil (Table IV, p. 32). Following a single desorption, 5.8-36.6% of the previously adsorbed radioactivity was desorbed from the clay soil (across all application levels), 32.4-103% was desorbed from the sand soil, 18.7-32.9% was desorbed from the sandy loam soil, and 4.7-15.7% was desorbed from the Timmerman sandy loam soil.

The stability of the parent compound in the soil:solution slurries following the adsorption and desorption phases was not confirmed; [^{14}C]residues were not characterized (see Comment #1).

Material balances (based on LSC analysis of individual replicates) across all application rates were 97.1-104.4% for the Arkansas clay soil samples, 92.7-101% for the Georgia sand soil samples, 95.5-100% for the sandy loam soil samples, and 90.6-94.7% for the Timmerman sandy loam soil samples (Tables XIII-XVI, pp. 41-44).

COMMENTS

1. It could not be confirmed that the parent compound was stable throughout the definitive study; [^{14}C]residues in the desorption supernatant were not characterized. Data from an independent stability study indicated that the parent compound was stable following a 36-hour adsorption period; 96.6-100% of the applied radioactivity was parent (Table III, p. 31). A desorption phase was not conducted in the independent stability study.

2. For the desorption phase of the definitive study, the amount of pesticide-free 0.01 M $CaCl_2$ added to the soil remaining from the adsorption phase was 5 mL less than the volume decanted following the adsorption phase. The study author stated that the volumes added were inadvertently 5 mL less because the volume of the solution removed for analysis following the adsorption phase was accounted for (p. 25).

3. The soil series names for three of the soils used in the study were not reported.

4. Only three concentrations were used to plot the desorption isotherm for the sand soil (Figure 11, p. 56). The study author stated that the results from the highest concentration (1.2 mg/L) were omitted from regression analysis due to the low levels of residues calculated to be in the soil (p. 22). At least four concentrations are necessary to accurately determine Freundlich isotherms and $K_{ads/des}$ values.

5. Method detection limits were reported for LSC analysis, but were not reported for HPLC analysis. Both limits of quantitation and detection should be reported to allow the reviewer to evaluate the adequacy of the test method for the determination of the test compound.

6. It could not be determined whether one of the soils used in the study was the same type of soil used in the aerobic metabolism study.

7. The study author did not indicate whether the definitive study was conducted in darkness; however, the test containers were placed in an environmental chamber (p. 13). The study author stated that the preliminary study was conducted in darkness.

8. The study author stated that, after LSC analysis of the aqueous desorption solution, adequate material balances for the sand and Timmerman sandy loam soils was obtained; therefore, these soils were not combusted to determine bound residues (p. 18).

Table I. Soil characteristics of Arkansas clay, Georgia sand, Sandy Loam and Timmerman sandy loam.

Soil Characteristics (0 to 9 inches)		Arkansas	Georgia	Sandy Loam	Timmerman
Classification		Clay	Sand	Sandy loam	Sandy loam
% Sand		16	92	56	66
% Silt		34	2	36	27
% Clay		50	6	8	7
% Organic Matter		1.6	1.3	3.5	0.9
% Organic Carbon[a]		0.941	0.765	2.06	0.529
pH		7.0	6.7	6.3	7.4
Bulk Density (disturbed) g/cc		1.09	1.35	0.94	1.28
Cation Exchange Capacity (meq/100 g)		34.9	4.3	11.9	14.4
Exchangeable Cations (ppm)					
	Calcium	61.6	47	29.4	58.9
	Magnesium	25.3	19.6	14	19
	Sodium	1.3	1.8	0.9	0.7
	Potassium	2.2	1.4	3.8	5.9
	Hydrogen	9.6	30.1	51.8	15.5
Field Moisture Capacity at 1/3 Bar (%)		30	7.3	39.1	12.5

Soil analysis was performed by Agvise Laboratories, Northwood, North Dakota.

[a] Calculated from % organic matter using the formula: % organic carbon = % organic matter/1.7. (Black *et al.*, 1965)

Table II. Measured concentrations of 2,4-DP-p concentrations during the preliminary (equilibrium determination) test.[a]

Time (Hours)	Concentration (mg/L)[b]	Time (Hours)	Concentration (mg/L)[b]
	ARKANSAS		**GEORGIA**
5	1.09	5	1.13
18[c]	1.04	18[c]	1.14
24	1.05	24	1.09
	SANDY LOAM		**TIMMERMAN**
5	0.943	5	1.11
18[c]	0.939	18[c]	1.15
24	0.898	24	1.12

[a] Calculated values are based on unrounded data rather than the rounded numbers presented here. Apparent errors in calculation may result from using rounded values.

[b] Initial concentration was 1.2 mg/L.

[c] Time selected for equilibration of 2,4-DP-p with this soil.

Table III. Stability of 2,4-DP-p as determined by HPLC-RAM after 36 hours of shaking.

	Sample ID	% of Initial Radioactivity in Aqueous Portion[a]	Measured Concentration (mg/L)[a]	Radioactivity Distribution (% Parent)
		Arkansas clay		
Arkansas Clay	Rep. 1	90.9	1.07	100
	Rep. 2	87.1	1.02	100
	Rep. 3	87.1	1.02	100
		Georgia sand		
Georgia Sand	Rep. 1	91.1	1.07	100
	Rep. 2	91.5	1.08	100
	Rep. 3	94.2	1.11	100
		Sandy loam		
Sandy Loam	Rep. 1	73.8	0.867	100
	Rep. 2	70.7	0.831	100
	Rep. 3	72.7	0.850	97.8
		Timmerman sandy loam		
Timmerman Sandy Loam	Rep. 1	89.8	1.06	100
	Rep. 2	96.8	1.14	100
	Rep. 3	91.2	1.07	96.6

[a] Determined by Liquid Scintillation Counting (LSC).

[b] Determined by HPLC-RAM. Initial concentration prior to equilibration was 1.2 mg/mL.

Table IV. Summary of mean adsorption and desorption results from isotherm tests for 2,4-DP-p.[a,b]

	Adsorption			Desorption		
Soil-Less Control (mg/L)	Aqueous Conc. (mg/L)	Soil Conc.[c] (mg/kg)	%Ads.	Aqueous Conc. (mg/L)	Soil Conc.[c] (mg/kg)	%Des.
			Arkansas clay			
1.22	1.05	0.835	13.7	0.178	0.560	33.2
0.620	0.531	0.443	14.3	0.0947	0.283	36.6
0.309	0.260	0.247	16.0	0.0410	0.192	22.0
0.156	0.129	0.135	17.3	0.0161	0.127	5.78
			Georgia sand			
1.22	1.17	0.252	4.14	0.110	0.0190	103
0.620	0.579	0.207	6.67	0.0573	0.0790	61.8
0.309	0.285	0.118	7.66	0.0280	0.0567	53.2
0.156	0.141	0.076	9.74	0.0126	0.0515	32.4
			Sandy loam			
1.22	0.912	1.52	25.0	0.212	1.02	32.9
0.620	0.444	0.882	28.4	0.107	0.624	29.4
0.309	0.217	0.462	29.9	0.0500	0.345	25.3
0.156	0.105	0.253	32.4	0.0223	0.205	18.7
			Timmerman sandy loam			
1.22	1.13	0.417	6.85	0.104	0.359	13.2
0.620	0.562	0.290	9.35	0.0553	0.245	15.7
0.309	0.283	0.130	8.41	0.0267	0.113	14.1
0.156	0.143	0.0673	8.63	0.0124	0.0636	4.71

a Calculated values are based on unrounded data rather than the rounded numbers presented here. Apparent errors in calculation may result from using rounded values.

b Test solutions were prepared with theoretical concentrations of 1.20, 0.600, 0.300, and 0.150 mg/L. Measured solution concentrations (LSC) prior to addition to soil were 1.24, 0.628, 0.315, and 0.160 mg/L, repectively.

c Calculated from aqueous concentration.

Table V. Measured aqueous concentrations, calculated soil concentrations and linear regression results for adsorption of 2,4-DP-p to Arkansas Clay during isotherm testing

Initial Concentration[a] (mg/L)	Measured Aqueous Concentration (mg/L)	Calculated Soil Concentration (mg/kg)		
1.22 mg/L				
Replicate 1	1.03	0.910		
Replicate 2	1.06	0.795		
Replicate 3	1.06	0.800		
Mean	1.05	0.835		
Standard Deviation	0.0130	0.0650		
0.620 mg/L			LOG (Ce)	LOG (Cs)
Replicate 1	0.561	0.295	0.0208	-0.0783
Replicate 2	0.518	0.510	-0.275	-0.353
Replicate 3	0.515	0.525	-0.586	-0.608
Mean	0.531	0.443	-0.889	-0.870
Standard Deviation	0.0257	0.129		
0.309 mg/L			Slope (1/n)	0.865
			Y-intercept (log K)	-0.104
Replicate 1	0.265	0.220	Coefficient of Determination	0.999
Replicate 2	0.253	0.280	(r^2)	
Replicate 3	0.261	0.240		
Mean	0.260	0.247		
Standard Deviation	0.00611	0.0306		
			n	1.16
0.156 mg/L			K	0.788
			Koc	83.7
Replicate 1	0.130	0.130		
Replicate 2	0.130	0.130		
Replicate 3	0.127	0.144		
Mean	0.129	0.135		
Standard Deviation	0.00167	0.00837		

[a] Concentration in soil-less control

Table VI. Measured aqueous concentrations, calculated soil concentrations and linear regression results for desorption of 2,4-DP-p from Arkansas clay during isotherm testing.

Initial Concentration[a] (mg/L)	Measured Aqueous Concentration (mg/L)	Calculated Soil Concentration (mg/kg)		
1.22 mg/L				
Replicate 1	0.170	0.662		
Replicate 2	0.178	0.523		
Replicate 3	0.185	0.496		
Mean	0.178	0.560		
Standard Deviation	0.00751	0.0894		
0.620 mg/L			LOG (C_1)	LOG (Cd)
Replicate 1	0.0880	0.180	-0.750	-0.252
Replicate 2	0.0980	0.328	-1.02	-0.548
Replicate 3	0.0980	0.341	-1.39	-0.717
Mean	0.0947	0.283	-1.79	-0.896
Standard Deviation	0.00577	0.0899		
0.309 mg/L			Slope (1/n)	0.590
			Y-intercept (log K)	0.128
Replicate 1	0.0410	0.168	Coefficient of Determination	0.951
Replicate 2	0.0440	0.208	(r^2)	
Replicate 3	0.0380	0.199		
Mean	0.0410	0.192		
Standard Deviation	0.00300	0.0213		
			n	1.70
0.156 mg/L			K`	1.34
			K`oc	143
Replicate 1	0.0154	0.126		
Replicate 2	0.0169	0.119		
Replicate 3	0.0159	0.136		
Mean	0.0161	0.127		
Standard Deviation	0.000764	0.00885		

[a] Concentration in soil-less control

Table VII. Measured aqueous concentrations, calculated soil concentrations and linear regression results for adsorption of 2,4-DP-p to Georgia sand during isotherm testing.

Intial Concentration[a] (mg/L)	Measured Aqueous Concentration (mg/L)	Calculated Soil Concentration (mg/kg)		
1.22 mg/L				
Replicate 1	1.14	0.360		
Replicate 2	1.17	0.235		
Replicate 3	1.18	0.160		
Mean	1.17	0.252		
Standard Deviation	0.0202	0.101		
0.620 mg/L			LOG (Ce)	Log (Cs)
Replicate 1	0.578	0.210	0.0666	-0.599
Replicate 2	0.578	0.210	-0.238	-0.685
Replicate 3	0.580	0.200	-0.545	-0.927
Mean	0.579	0.207	-0.851	-1.12
Standard Deviation	0.00115	0.00577		
0.309 mg/L			Slope (1/n)	0.589
			Y-intercept (log K)	-0.602
Replicate 1	0.283	0.130	Coefficient of Determination	0.971
Replicate 2	0.282	0.135	(r^2)	
Replicate 3	0.291	0.0900		
Mean	0.285	0.118		
Standard Deviation	0.00493	0.0247		
			n	1.70
0.156 mg/L			K	0.250
			Koc	32.7
Replicate 1	0.142	0.0700		
Replicate 2	0.140	0.0800		
Replicate 3	0.140	0.0780		
Mean	0.141	0.0760		
Standard Deviation	0.00106	0.00529		

[a] Concentration in soil-less control

Table VIII. Measured aqueous concentrations, calculated soil concentrations and linear regression results for desorption of 2,4-DP-p from Georgia sand during isotherm testing.

Initial Concentration[a] (mg/L)	Measured Aqueous Concentration (mg/L)	Calculated Soil Concentration (mg/kg)		
1.22 mg/L[b]				
Replicate 1	0.110	0.124		
Replicate 2	0.109	0.00950		
Replicate 3	0.112	-0.760[c]		
Mean	0.110	0.0665		
Standard Deviation	0.00153	NR		
0.620 mg/L			LOG (C_1)	LOG (Cd)
Replicate 1	0.0580	0.0790		
Replicate 2	0.0570	0.0837	-1.24	-1.10
Replicate 3	0.0570	0.0743	-1.55	-1.25
Mean	0.0573	0.0790	-1.90	-1.29
Standard Deviation	0.000577	0.00475		
0.309 mg/L			Slope (1/n)	0.279
			Y-intercept (log K)	-0.776
Replicate 1	0.0290	0.0630	Coefficient of Determination	0.888
Replicate 2	0.0280	0.0725	(r^2)	
Replicate 3	0.0270	0.0345		
Mean	0.0280	0.0567		
Standard Deviation	0.001	0.0198		
			n	3.59
0.156 mg/L			K`	0.167
			K`oc	21.9
Replicate 1	0.0130	0.0438		
Replicate 2	0.0125	0.0556		
Replicate 3	0.0122	0.0552		
Mean	0.0126	0.0515		
Standard Deviation	0.000404	0.00672		

[a] Concentration in soil-less control.
[b] The results from this concentration were omitted from regression analysis because of the low calculated soil concentration.
[c] Value was excluded from calculation of mean.

Table IX. Measured aqueous concentrations, calculated soil concentrations and linear regression results for adsorption of 2,4-DP-p to Sandy loam during isotherm testing.

Intial Concentration[a] (mg/L)	Measured Aqueous Concentration (mg/L)	Calculated Soil Concentration (mg/kg)		
1.216 mg/L				
Replicate 1	0.928	1.44		
Replicate 2	0.913	1.51		
Replicate 3	0.896	1.60		
Mean	0.912	1.52		
Standard Deviation	0.0160	0.0801		
0.620 mg/L			LOG (Ce)	LOG (Cs)
Replicate 1	0.444	0.880	-0.0398	0.181
Replicate 2	0.456	0.820	-0.353	-0.0547
Replicate 3	0.431	0.945	-0.664	-0.336
Mean	0.444	0.882	-0.977	-0.597
Standard Deviation	0.0125	0.0625		
0.309 mg/L			Slope (1/n)	0.838
			Y-intercept (log K)	0.225
Replicate 1	0.219	0.450	Coefficient of Determination	0.999
Replicate 2	0.218	0.455	(r^2)	
Replicate 3	0.213	0.480		
Mean	0.217	0.462		
Standard Deviation	0.00321	0.0161		
			n	1.19
0.156 mg/L			K	1.68
			Koc	81.5
Replicate 1	0.106	0.250		
Replicate 2	N/A	N/A		
Replicate 3	0.105	0.255		
Mean	0.105	0.253		
Standard Deviation	0.000778	0.00389		

[a] Concentration in soil-less control

Table X. Measured aqueous concentrations, calculated soil concentrations and linear regression results for desorption of 2,4-DP-p from Sandy loam isotherm testing.

Initial Concentration[a] (mg/L)	Measured Aqueous Concentration (mg/L)	Calculated Soil Concentration (mg/kg)		
1.216 mg/L				
Replicate 1	0.210	0.959		
Replicate 2	0.214	1.01		
Replicate 3	0.213	1.09		
Mean	0.212	1.02		
Standard Deviation	0.00208	0.0659		
0.620 mg/L			LOG (C_1)	LOG (Cd)
Replicate 1	0.117	0.576	-0.673	0.00817
Replicate 2	0.102	0.589	-0.972	-0.205
Replicate 3	0.101	0.706	-1.30	-0.462
Mean	0.107	0.624	-1.65	-0.688
Standard Deviation	0.00896	0.0717		
0.309 mg/L			Slope (1/n)	0.717
			Y-intercept (log K)	0.487
Replicate 1	0.0520	0.326	Coefficient of Determination	0.999
Replicate 2	0.0470	0.352	(r^2)	
Replicate 3	0.0510	0.357		
Mean	0.0500	0.345		
Standard Deviation	0.00265	0.0170		
			n	1.40
0.156 mg/L			K`	3.07
			K`oc	149
Replicate 1	0.0211	0.208		
Replicate 2	NA	NA		
Replicate 3	0.0234	0.203		
Mean	0.0223	0.205		
Standard Deviation	0.00163	0.00382		

[a] Concentration in soil-less control

Table XI. Measured aqueous concentrations, calculated soil concentrations and linear regression results for adsorption of 2,4-DP-p to Timmerman sandy loam during isotherm testing.

Intial Concentration[a] (mg/L)	Measured Aqueous Concentration (mg/L)	Calculated Soil Concentration (mg/kg)		
1.22 mg/L				
Replicate 1	1.12	0.500		
Replicate 2	1.14	0.365		
Replicate 3	1.14	0.385		
Mean	1.13	0.417		
Standard Deviation	0.0146	0.0729		
0.620 mg/L			LOG (Ce)	LOG (Cs)
Replicate 1	0.565	0.275	0.0541	-0.380
Replicate 2	0.558	0.310	-0.250	-0.538
Replicate 3	0.563	0.285	-0.548	-0.886
Mean	0.562	0.290	-0.846	-1.17
Standard Deviation	0.00361	0.018		
0.309 mg/L			Slope (1/n)	0.9075
			Y-intercept (log K)	-0.383
Replicate 1	0.284	0.125	Coefficient of Determination	0.979
Replicate 2	0.278	0.155	(r^2)	
Replicate 3	0.287	0.110		
Mean	0.283	0.130		
Standard Deviation	0.00458	0.0229		
			n	1.10
0.156 mg/L			K	0.414
			Koc	78.2
Replicate 1	0.141	0.0750		
Replicate 2	0.146	0.0500		
Replicate 3	0.141	0.0770		
Mean	0.143	0.0673		
Standard Deviation	0.00301	0.0150		

[a] Concentration in soil-less control

Table XII. **Measured aqueous concentrations, calculated soil concentrations and linear regression results for desorption of 2,4-DP-p from Timmerman sandy loam during isotherm testing.**

Initial Concentration[a] (mg/L)	Measured Aqueous Concentration (mg/L)	Calculated Soil Concentration (mg/kg)		
1.22 mg/L				
Replicate 1	0.113	0.396		
Replicate 2	0.106	0.303		
Replicate 3	0.0940	0.377		
Mean	0.104	0.359		
Standard Deviation	0.00961	0.0489		
0.620 mg/L			LOG (C_1)	LOG (Cd)
Replicate 1	0.0580	0.219	-0.982	-0.445
Replicate 2	0.0540	0.269	-1.26	-0.611
Replicate 3	0.0540	0.246	-1.57	-0.948
Mean	0.0553	0.245	-1.91	-1.20
Standard Deviation	0.00231	0.0255		
0.309 mg/L			Slope (1/n)	0.839
			Y-intercept (log K)	0.399
Replicate 1	0.0260	0.111	Coefficient of Determination	0.991
Replicate 2	0.0250	0.144	(r^2)	
Replicate 3	0.0290	0.0835		
Mean	0.0267	0.113		
Standard Deviation	0.00208	0.0301		
			n	1.19
0.156 mg/L			K`	2.51
			K`oc	474
Replicate 1	0.0114	0.0751		
Replicate 2	0.0117	0.0506		
Replicate 3	0.0140	0.0650		
Mean	0.0124	0.0636		
Standard Deviation	0.00142	0.0123		

[a] Concentration in soil-less control

Table XIII. Radioactive material balance for 2,4-DP-p using Arkansas clay. [a]

Rep.	DPM in Adsorption (5 ml)	Total DPM in Solution Adsorption[b]	DPM in Desorption (5 ml)	Total DPM in Solution Desorption[b]	DPM in Extract (5 ml)[b,c]	Total DPM Extraction	Total DPM in Soil Burns	Total DPM Recovered	% Recovery
Initial concentration 1.22 mg/L (dpm 554000), based on soil-less control									
1	58700	423000	9650	69500	2100	15100	31800	539400	97.4
2	60000	432000	10100	72700	2210	15900	30600	551000	99.5
3	59900	432000	10500	75400	2360	17000	32900	557000	100.5
Initial concentration 0.620 mg/L (dpm 282000), based on soil-less control									
1	31900	229000	5020	36200	1150	8270	20400	294000	104.4
2	29400	212000	5570	40100	1180	8500	20100	280000	99.5
3	29300	211000	5580	40200	1180	8470	20500	280000	99.3
Initial concentration 0.309 mg/L (dpm 140000), based on soil-less control									
1	15100	109000	2310	16700	472	3400	13600	142000	101.4
2	14300	103000	2510	18100	500	3600	11900	137000	97.6
3	14900	107000	2140	15400	443	3200	12000	138000	98.1
Initial concentration 0.156 mg/L (dpm 70800), based on soil-less control									
1	7400	53300	874	6300	164	1180	9530	70300	99.3
2	7370	53100	958	6900	189	1360	8290	69600	98.4
3	7220	52000	905	6520	173	1240	8980	68700	97.1

[a] Calculated values are based on unrounded data rather than the rounded numbers presented here. Apparent errors in calculation may result from using rounded values.

[b] Total volume in test system 40 mL

[c] In order to ensure that adequate material balance would be obtained in the clay soil, the soil was further extracted with 0.01M $CaCl_2$ and the soil was subsequently combusted for [^{14}C]residues

Table XIV. Radioactive material balance for 2,4-DP-p using Georgia sand. [a]

Rep.	DPM in Adsorption (5 ml)	Total DPM in Solution Adsorption [b]	DPM in Desorption (5 ml)	Total DPM in Solution Desorption [b]	DPM in Extract (5 ml)	Total DPM Extraction	Total DPM in Soil Burns	Total DPM Recovered	% Recovery
Initial concentration 1.22 mg/L (dpm 554000), based on soil-less control									
1	64900	494000	6230	47300	NA	NA	NA	541000	97.6
2	66400	504000	6180	47000	NA	NA	NA	551000	99.5
3	67200	511000	6390	48500	NA	NA	NA	559000	101.0
Initial concentration 0.620 mg/L (dpm 282000), based on soil-less control									
1	32800	249500	3300	25100	NA	NA	NA	275000	97.5
2	32800	249400	3240	24600	NA	NA	NA	274000	97.2
3	32900	250000	3220	24500	NA	NA	NA	275000	97.4
Initial concentration 0.309 mg/L (dpm 140000), based on soil-less control									
1	16000	122000	1640	12500	NA	NA	NA	134000	95.9
2	16000	122000	1570	11900	NA	NA	NA	133000	95.2
3	16500	125000	1540	11700	NA	NA	NA	137000	97.8
Initial concentration 0.156 mg/L (dpm 70800), based on soil-less control									
1	8040	61130	738	5610	NA	NA	NA	66700	94.3
2	7930	60200	709	5390	NA	NA	NA	65600	92.7
3	7970	60600	691	5250	NA	NA	NA	65800	93.0

[a] Calculated values are based on unrounded data rather than the rounded numbers presented here. Apparent errors in calculation may result from using rounded values.

[b] Total volume in test system 40 mL

NA Not applicable. The extraction and combustion steps were not performed with the Georgia sand soil since adequate material balance was obtained after the desorption step.

Table XV. Radioactive material balance for 2,4-DP-p using Sandy loam. [a]

Rep.	DPM in Adsorption (5 ml)	Total DPM in Solution Adsorption[b]	DPM in Desorption (5 ml)	Total DPM in Solution Desorption[b]	DPM in Extract (5 ml)[b,c]	Total DPM Extraction	Total DPM in Soil Burns	Total DPM Recovered	% Recovery
Initial concentration 1.22 mg/L (dpm 554000), based on soil-less control									
1	52700	379000	11900	85800	3430	24700	49600	540000	97.4
2	51800	373000	12100	87400	3580	25800	59800	546000	98.6
3	50800	366000	12100	87000	3580	25800	55800	535000	96.5
Initial concentration 0.620 mg/L (dpm 282000), based on soil-less control									
1	25200	182000	6620	47600	1910	13800	35500	279000	98.8
2	25900	186000	5780	41600	1640	11800	34100	274000	97.2
3	24500	176000	5720	41200	1690	12100	42900	272000	96.6
Initial concentration 0.309 mg/L (dpm 140000), based on soil-less control									
1	12400	89400	2940	21100	903	6500	19100	136000	97.1
2	12400	89100	2650	19100	867	6250	19500	134000	95.5
3	12100	87000	2880	20700	862	6200	20800	135000	96.2
Initial concentration 0.156 mg/L (dpm 70800), based on soil-less control									
1	6040	43500	1200	8610	384	2760	16000	70900	100
2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
3	5960	42900	1330	9580	381	2740	13200	68400	96.6

[a] Calculated values are based on unrounded data rather than the rounded numbers presented here. Apparent errors in calculation may result from using rounded values.

[b] Total volume in test system 40 mL

[c] In order to ensure that adequate material balance would be obtained in the sandy loam soil, the soil was further extracted with 0.01 M $CaCl_2$ and the soil was subsequently combusted for [^{14}C]residues.

Table XVI. Radioactive material balance for 2,4-DP-p using Timmerman sandy loam. [a]

Rep.	DPM in Adsorption (5 ml)	Total DPM in Solution Adsorption[b]	DPM in Desorption (5 ml)	Total DPM in Solution Desorption[b]	DPM in Extract (5 ml)	Total DPM Extraction	Total DPM in Soil Burns	Total DPM Recovered	% Recovery
Initial concentration 1.22 mg/L (dpm 554000), based on soil-less control									
1	63400	469000	6390	47300	NA	NA	NA	516000	93.2
2	64900	480000	6040	44700	NA	NA	NA	525000	94.7
	64700	478000	5330	39400	NA	NA	NA	518000	93.5
Initial concentration 0.620 mg/L (dpm 282000), based on soil-less control									
1	32100	237000	3310	24500	NA	NA	NA	262000	92.9
2	31700	234000	3090	22900	NA	NA	NA	257000	91.3
3	32000	237000	3080	22800	NA	NA	NA	260000	92.1
Initial concentration 0.309 mg/L (dpm 140000), based on soil-less control									
1	16100	119000	1480	11000	NA	NA	NA	130000	92.9
2	15800	117000	1420	10500	NA	NA	NA	127000	90.8
3	16300	121000	1630	12100	NA	NA	NA	133000	94.7
Initial concentration 0.156 mg/L (dpm 70800), based on soil-less control									
1	8020	59300	645	4770	NA	NA	NA	64100	90.6
2	8280	61300	662	4900	NA	NA	NA	66200	93.5
3	7980	59100	793	5870	NA	NA	NA	64900	91.8

[a] Calculated values are based on unrounded data rather than the rounded numbers presented here. Apparent errors in calculation may result from using rounded values.

[b] Total volume in test system 40 mL

NA Not applicable. The extraction and combustion steps were not performed with the Timmerman sandy loam soil since adequate material balance was obtained after the desorption step.

Figure 1. Chemical structure of (R)-2-(2,4-Dichlorophenoxy)propionic acid-(phenyl-U-^{14}C) (2,4-DP-p).

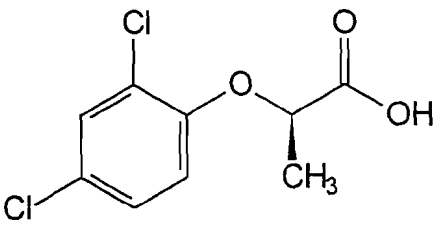
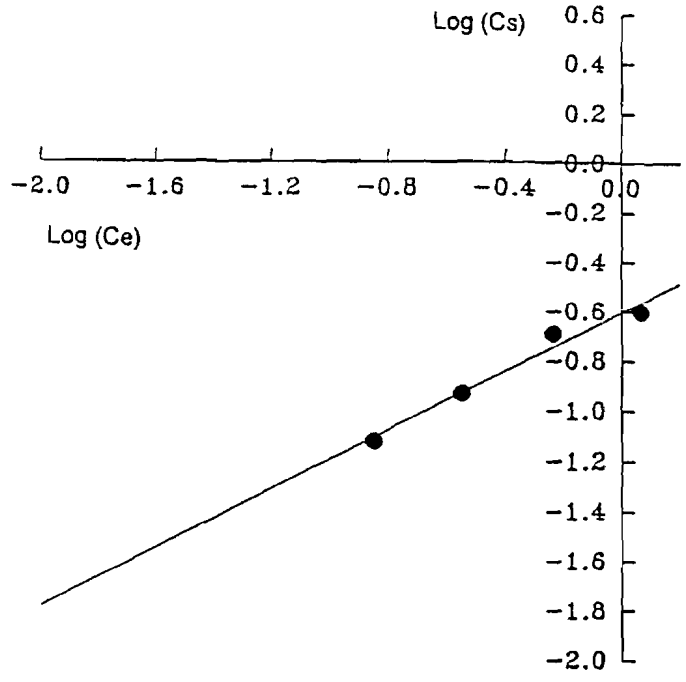
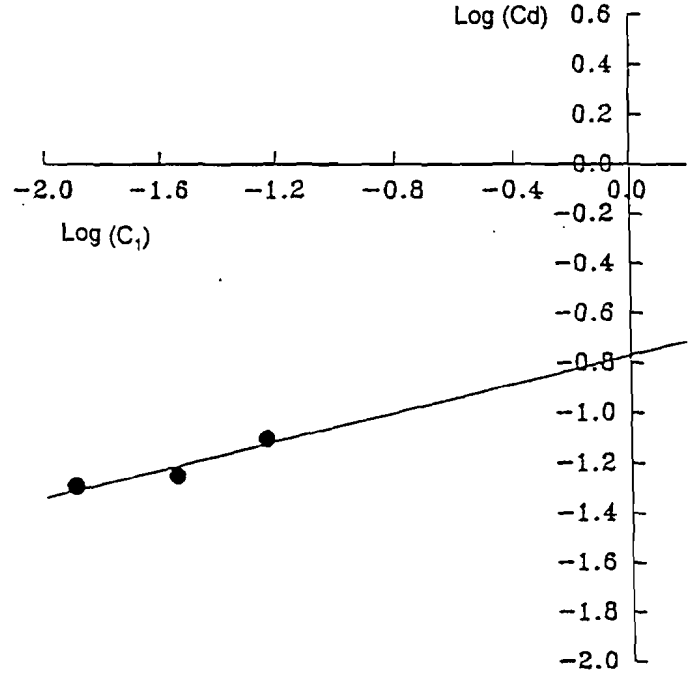


Figure 11. Adsorption and desorption isotherms of 2,4-DP-p in Georgia sand.



Adsorption



Desorption

2.4.2 Test Conditions. The test containers used for this study consisted of 50-mL Pyrex® glass centrifuge tubes with Teflon®-lined caps. The amounts of soil and water used were selected so as to fill the test vessels completely to avoid possible volatilization of test material. Individual test containers were identified by project number, test material name, replicate number, test phase, and nominal concentration. All test containers were shaken on a Labline Orbital Shaker in an environmental chamber designed to maintain a constant temperature of 20 ± 2 °C.

2.5 Calculation of Aqueous Concentrations

The calculation used in determining the concentration of ^{14}C-residues in the aqueous test solutions and samples was:

$$\text{Test material (mg/L)} = \frac{\text{Net dpm}}{\text{effective specific activity of } ^{14}C\text{-material} \times \text{sample size}}$$

where

Net dpm	=	disintegrations per minute calculated by the instrument after background subtraction and correction for counting efficiency
Sample size	=	Sample volume (L)
Effective specific activity	=	1.14×10^7 dpm/mg for 2,4-DP-p (after isotopic dilution into dosing stock)

3.0 PRELIMINARY TEST

3.1 Test Solution Preparation

A 2,4-DP-p test solution was prepared for preliminary testing by combining 2.35 mL of the 1.02 mg/mL radiolabeled stock solution and diluting to 2000 mL with sterile 0.01 M $CaCl_2$. This produced a test solution with a theoretical concentration of 1.20 mg/L. Analysis of the solution in triplicate by liquid scintillation counting resulted in a measured concentration of 1.21 mg/L.

3.2 Preliminary Test Procedure

Preliminary testing was performed to establish solution:soil ratios and equilibration times for the isotherm testing. Testing was performed using the 1.20 mg/L solution of 2,4-DP-p in 0.01 M

$CaCl_2$ and a 5:1 solution to soil ratio. For each soil, nine test systems containing the test material solution and soil, and nine soil-less controls were established.

For each soil, nine 8-gram (dry weight) aliquots of soil were weighed into 50-mL Pyrex® glass centrifuge tubes with Teflon®-lined caps. A 40-mL aliquot of the solution was then added to each tube, providing a solution to soil ratio of 5:1. In addition, nine centrifuge tubes were prepared containing 40 mL of the test solution to serve as soil-less controls. All tubes were shaken on a Labline Orbital Shaker operating at approximately 125 revolutions per minute (rpm) and were maintained in the dark. Three tubes containing each soil and three soil-less control tubes were removed from the shaker table at intervals of 5, 18, and 24 hours. The tubes were centrifuged (Beckman GSGR centrifuge) at approximately 1000 rpm for 30 minutes to separate the soil and aqueous phases. This centrifuging regime produced a clear supernatant for all soils, with some organic particulate matter (e.g., plant fragments) floating on the surface.

A 5-mL aliquot of the supernatant was removed from each centrifuge tube using a digital pipet with disposable plastic tips and transferred into a scintillation vial. A clean tip was used for each sample. Approximately 15 mL of Monophase® scintillation cocktail was then added to the vials and the contents mixed by shaking. After shaking, the vials were placed into a Packard Tricarb 1600 CA liquid scintillation counter for quantitation of the aqueous concentration of 2,4-DP-p. The results of this analysis were used to establish an equilibrium time (i.e., a plateau in aqueous concentration) and a solution:soil ratio (to result in approximately 50% of the test material in solution following equilibration) for the isotherm test.

3.3 Preliminary Test Analysis

All radioactivity analyses were performed using a Packard Tricarb 1600 CA liquid scintillation counter (LSC) calibrated with factory-prepared standards. Counting efficiencies of all experimental samples were determined using an external standard and a factory-prepared calibration curve (Beckman Instruments). All test samples were counted for a maximum of 5 minutes (Packard LSC) or until a 2 sigma error of 5% was attained. Using this criterion, it was determined at the 90% confidence level that all samples of 31 cpm (background 25.72 cpm) had

an associated error of 10%. This percentage was the maximum acceptable error and was associated with the minimum net cpm of a sample. The counting error decreased as the sample activity increased. The minimum detectable ^{14}C-residue concentration was dependent on the counting efficiency, sample size (milliliters or grams) and the acceptable minimum net cpm. For [^{14}C]2,4-DP-p solution prepared using the dosing stock, with an effective specific activity of 11,353.4 dpm/µg, the detection limit using 5-mL aqueous samples and a counting efficiency of 94%, was 0.581 µg/L.

3.4 Preliminary Test Results

Following 5, 18, and 24 hours of agitation, the measured aqueous concentrations of 2,4-DP-p exposed to Arkansas clay were 1.09, 1.04, and 1.05 mg/L, respectively. When exposed to Georgia sand, the measured aqueous concentrations were 1.13, 1.14, and 1.09 mg/L, respectively. Using Sandy loam, the measured aqueous concentrations were 0.943, 0.939, and 0.898 mg/L, respectively, and for using Timmerman sandy loam, the measured aqueous concentrations were 1.11, 1.15, and 1.12 mg/L, respectively (Table II). Graphical presentation of the data (Figures 2 to 5) indicated a plateau in aqueous concentration was established within 5 hours and remained constant through 24 hours. Thus, 18 hours was selected as an equilibrium time for the adsorption phase of the isotherm test. Because little of the test material sorbed to the soils using a 5:1 solution ratio, that ratio was also used in the isotherm tests.

4.0 STABILITY TEST

4.1 Test Solution Preparation

A 2,4-DP-p test solution was prepared for stability testing by combining 1.15 mL of the 1.02 mg/mL radiolabeled stock solution and diluting to 1000 mL with sterile 0.01 M $CaCl_2$. This produced a test solution with a theoretical concentration of 1.20 mg/L. LSC analysis of the prepared solution (in triplicate) resulted in a measured concentration of 1.18 mg/L.

4.2 Stability Test Procedure

A stability test was performed in triplicate in 0.01 M $CaCl_2$ with solution to soil ratios of 5:1 for 2,4-DP-p to verify that the test material did not degrade during the equilibration periods.

Three aliquots of each soil (8 g dry weight) were placed in 50-mL Pyrex® glass centrifuge tubes with Teflon®-lined screw-caps. A 40-mL aliquot of the test solution was added to each tube, producing a 5:1 solution:soil ratio. All tubes were shaken on a Labline Orbital Shaker (Model 3590) operating at approximately 125 rpm. After 36 hours of shaking, the tubes were removed and the aqueous phase separated, and the aqueous phase was analyzed by high performance liquid chromatography with radiometric detection (HPLC-RAM). Because a large proportion (70.7 to 96.8%) of the test material was in the aqueous phase, the soil was not analyzed.

4.3 Stability Test Analysis

Aqueous samples were subjected to compound-specific analysis by HPLC-RAM for 2,4-DP-p. Instrumentation consisted of a Waters 510 solvent pump, a Hewlett-Packard Model 1050 autosampler and a Radiomatic Model A 280 radioisotope detector.

The HPLC analysis was conducted using the following instrumental conditions:

Column: Metachem Spherisorb ODS-2, 250 mm (length) x 4.6 mm (I.D.), PS 5 µm

Mobile Phase: A: 0.1% trifluoroacetic acid in reagent water
B: acetonitrile

Gradient Program:

Time (min)	A%	B%	Type
Initial	60	40	NA
20	60	40	Linear
30	40	60	Linear
31	0	100	Linear
36	0	100	Linear
37	60	40	Linear

Flow Rate: 1.0 mL/minute
Cocktail Type: Flo-Scint II

Cocktail Flow Rate: 3.0 mL/minute
Flow Cell Volume: 1000 µL
Injection Volume: 10, 100 or 200 µL

Introduction of samples and standards into the chromatographic system was performed by programmed injection.

4.4 Stability Test Results

Analysis of the prepared test solutions by LSC prior to equilibration resulted in a mean concentration of 1.20 mg/L for the 2,4-DP-p solution. The stability of 2,4-DP-p in Arkansas clay, Georgia sand, Sandy loam and Timmerman sandy loam was demonstrated by the high percent of parent material in the aqueous fractions from each of the soils, 96.6 to 100% of recovered radioactivity (Table III). Representative chromatograms from the aqueous phase samples appear in Figures 6 to 9.

5.0 ISOTHERM TEST

5.1 Test Solution Preparation

2,4-DP-p test solutions were prepared in sterile 0.01 M $CaCl_2$ at theoretical concentrations of 1.20, 0.600, 0.300, and 0.150 mg/L by combining 1.18, 0.600, 0.300, and 0.150 mL, respectively, of the 1.02 mg/mL radiolabeled stock solution and diluting to 1000 mL with 0.01 M $CaCl_2$. The solutions thus prepared were assayed in triplicate by liquid scintillation counting (LSC) in order to verify the concentration prior to use.

5.2 Isotherm Test Procedure

The isotherm test was performed in 0.01 M $CaCl_2$ with a 5:1 solution to soil ratio for all four soils. An equilibrium time of 18 hours was selected for each soil based on the results of the preliminary test.

Three aliquots (8 g dry weight) of each soil and 40 mL of test solution were added to separate test systems for each solution concentration. In addition, three soil-less controls and three soil blanks were prepared for each sample set. The entire sample set was shaken for

18 hours at approximately 125 rpm, followed by phase separation and sampling for radioassay as described in previous sections. The aqueous phase was carefully decanted from each tube containing soil, and the volume was measured. An effort was made to remove as much water as possible from the soil prior to desorption. Analysis of samples was conducted using the instruments and conditions described in Section 3.3.

The desorption phase of the test was performed by adding sterile 0.01 M $CaCl_2$ to all the centrifuge tubes containing each soil. The volume of 0.01 M $CaCl_2$ added was equal to the average volume recovered from the blank vessels in the adsorption phase. The 2,4-DP-p retained in the soil phase was allowed to desorb from the soil while shaking for 48 hours. The centrifuge tubes were removed from the shaker and the aqueous phase separated and analyzed as previously described.

After LSC analysis of the aqueous desorption solution, adequate material balance for the Georgia sand and Timmerman sandy loam was obtained and no further analysis was conducted with these soils. An additional desorption step was performed with the Arkansas clay and Sandy loam soil to remove further [^{14}C]residues. The aqueous phase from the first desorption step was carefully decanted from each tube containing these two soil types, and the volume was measured. A volume of sterile 0.01 M $CaCl_2$, equal to the volume removed, was added and remaining 2,4-DP-p was allowed to desorb from the soil by shaking at 125 rpm for 18 hours. The aqueous phase was separated and analyzed as previously described. The soil remaining in the centrifuge tubes was analyzed by soil combustion.

5.3 Soil Combustion

The quantity of [^{14}C]residues in the Arkansas clay and Sandy loam soil was determined by combustion of soil aliquots following the desorption phases of the isotherm testing for the purpose of determining material balance.

Samples were combusted in a Packard Model 307 sample oxidizer, and the resultant $^{14}CO_2$ was trapped in Carbosorb® solution to which Permafluor® scintillation cocktail was added.

K and 1/n were determined using the logarithmic transformation of the Freundlich equation:

$$\log\left[\frac{x}{m}\right] = \log K + \frac{1}{n} \log C_e$$

The desorption coefficient (K') was similarly calculated, substituting C_d for x/m and C_1 for C_e.

The sorption and desorption coefficients were also expressed as a function of the organic carbon content of the soils as:

$$K_{oc} = \frac{K}{\%C/100}$$

where:

%C = the percent organic carbon in the soil = % organic matter/1.7

Radioactive material balance was calculated by adding the dpm recovered from the aqueous phase in both the adsorption and desorption phases, and dpm from combusted soil (bound residues), and dividing by the radioactivity initially applied (based on dpm in soil-less controls).

5.5 Isotherm Test Results

Analysis of the test solutions prior to equilibration resulted in concentrations of 1.20, 0.600, 0.300 and 0.150 mg/L for the 2,4-DP-p test solutions. Corresponding soil-less control concentrations were 1.22, 0.620, 0.309, and 0.156 mg/L, respectively (Table IV). Comparison of the prepared test solution and soil-less control concentrations indicates that adsorption to the glass test vessels and Teflon®-lined caps did not occur.

Using the Arkansas clay, the mean concentrations of 2,4-DP-p remaining in solution following adsorption (C_e) were (in order of descending initial concentration) 1.05, 0.531, 0.260, and

PROTOCOL DEVIATIONS

1. The protocol states in section 5.2 that all glassware and the 0.01M $CaCl_2$ solution will be autoclaved prior to use to minimize the possibility of microbial degradation of the test material. For the preliminary phase of the test glassware was not autoclaved but the 0.01M $CaCl_2$ solution was sterilized. For the remaining phases of the test the glassware and 0.01M $CaCl_2$ solution were sterilized by autoclave prior to use.

2. The protocol states in section 5.8, paragraph two, that a volume of 0.01M $CaCl_2$ solution (equal to the aqueous phase removed after the adsorption phase) is added to the soil. Inadvertently, for each soil type, the volumes added to each soil were 5 mL less than the volume recovered because the volume removed for analysis after adsorption was not added.

These deviations are not expected to alter the results of this study.

SPRINGBORN LABORATORIES, INC.

David Wells 7 May 96

David Wells Date
Study Director